

Method of preparing lithium complex salts
for use in electrochemical cells

The invention relates to a method of preparing lithium
5 complex salts and to the use of these in electro-
chemical cells.

Lithium ion batteries are amongst the most promising
systems for mobile applications, the fields of applica-
10 tion extending from sophisticated electronic appliances
(e.g. mobile phones, camcorders) to batteries for
electrically driven motor vehicles.

These batteries consist of cathode, anode, separator
15 and a nonaqueous electrolyte. The cathodes used are
typically $\text{Li}(\text{MnMe}_2)_2\text{O}_4$, $\text{Li}(\text{CoMe}_2)\text{O}_2$, $\text{Li}(\text{CoNi}_x\text{Me}_2)\text{O}_2$ or
other lithium intercalation and insertion compounds.
Anodes can consist of lithium metal, carbon materials,
graphite, graphitic carbon materials or other lithium
20 intercalation and insertion compounds or alloy com-
pounds. The electrolyte used is in the form of solu-
tions comprising lithium salts such as LiPF_6 , LiBF_4 ,
 LiClO_4 , LiAsF_6 , LiCF_3SO_3 , $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ or $\text{LiC}(\text{CF}_3\text{SO}_2)_3$ and
mixtures of these in aprotic solvents.

25

The standard conducting lithium salts have various
drawbacks. Some conducting salts having low cycling
yields (e.g. LiBF_4). Other conducting salts have low
thermal stability (e.g. LiPF_6), and yet other conduct-
30 ing salts are not particularly suitable because of
their toxicity and poor environmental safety (e.g.
 LiAsF_6).

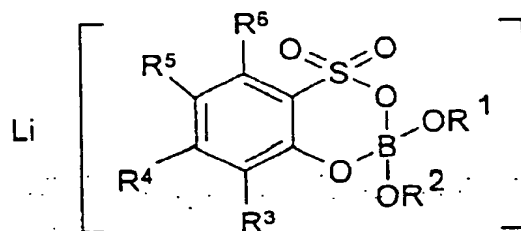
WO 98/07729 therefore describes a novel class of
35 conducting salts, the lithium borate complexes. These
compounds gave particularly good results in cycling
trials and proved especially stable. In combination
with other salts, these complexes exhibit a synergistic
stabilizing effect with respect to oxidation.

A description of lithium bis[5-fluoro-2-olato-benzene-sulfonato(2)-O,O']borate(1-) reveals a conducting salt which, on the basis of its properties, must be regarded as a very promising conducting salt for use in lithium ion batteries. It does, however, present the problem of the cost-intensive and complicated synthesis of the precursors.

The only previous literature reference (Speier, The Preparation and Properties of (Hydroxyorgano)-silanes and related compounds, J. Am. Chem. Soc. 74 (1952), 1003) on the synthesis of 2-hydroxybenzenesulfonic acids and its derivatives describes this as a laborious three-step procedure with overall yields in the range of between 40 and 70%.

It is therefore a feature of the present invention to provide a simple method for the synthesis of lithium complex salts.

This feature is achieved by a method of preparing lithium complex salts of the general formula



(I)

where

R^1 and R^2 are identical or different, are directly linked or not directly linked to one another via a single or double bond, each, individually or jointly, have the meaning of an aromatic ring from the group phenyl, naphthyl, anthracenyl or phenanthrenyl, which can be unsubstituted or mono- to

hexasubstituted by alkyl (C_1 to C_6), alkoxy groups (C_1 to C_6) or halogen (F, Cl, Br),

5 or each, individually or jointly, have the meaning of an aromatic heterocyclic ring from the group pyridyl, pyrazyl or pyrimidyl, which can be unsubstituted or mono- to tetrasubstituted by alkyl (C_1 to C_6), alkoxyl (C_1 to C_6) or halogen (F, Cl, Br),

10

or each, individually or jointly, have the meaning of an aromatic ring from the group hydroxybenzene-carboxyl, hydroxynaphthalenecarboxyl, hydroxybenzenesulfonyl and hydroxynaphthalenesulfonyl, which
15 can be unsubstituted or mono- to tetrasubstituted by alkyl (C_1 to C_6), alkoxy groups (C_1 to C_6) or halogen (F, Cl, Br),

R^3 - R^6 can each, individually or pairwise, being directly
20 linked or not directly linked to one another (i.e., are optionally directly linked to an adjacent ring substituent) via a single or double bond, have the following meaning:

25 1. alkyl (C_1 to C_6), alkyloxy (C_1 to C_6) or halogen (F, Cl, Br)

2. an aromatic ring from the groups

30 phenyl, naphthyl, anthracenyl or phenanthrenyl, which can be unsubstituted or mono- to hexasubstituted by alkyl (C_1 to C_6), alkoxy groups (C_1 to C_6) or halogen (F, Cl, Br),

35 pyridyl, pyrazyl or pyrimidyl, which can be unsubstituted or mono- to tetrasubstituted by alkyl (C_1 to C_6), alkoxyl (C_1 to C_6) or halogen (F, Cl, Br),

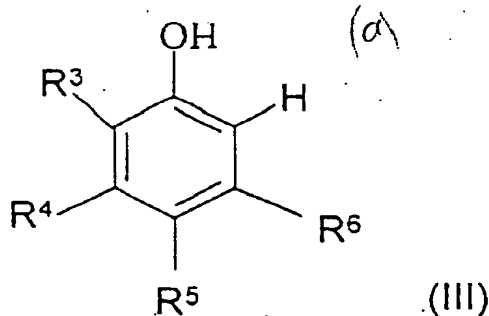
characterized in that

a) 3-, 4-, 5-, 6-substituted phenol (III) in a suitable solvent is admixed with chlorosulfonic acid,

b) the intermediate (IV) from a) is reacted with chlorotrimethylsilane, and the product is filtered and subjected to fractional distillation,

c) the intermediate (II) from b) is reacted with lithiumtetramethanolate borate(1-) in a suitable solvent and the end product (I) is isolated therefrom.

We have found that, starting from 3-, 4-, 5-, 6-substituted phenol (III), it is possible to prepare lithium complex salts in a 3-step synthesis. The starting material is a compound of the general formula:



R³-R⁶ can each, individually or pairwise, being directly linked or not directly linked to one another via a single or double bond, have the following meaning:

1. alkyl (C₁ to C₆), alkyloxy (C₁ to C₆) or halogen (F, Cl, Br)
2. an aromatic ring from the groups

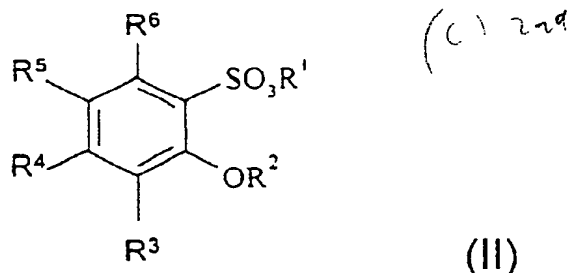
phenyl, naphthyl, anthracenyl or phenanthrenyl, which can be unsubstituted or mono- to hexasubstituted by

alkyl (C₁ to C₆), alkoxy groups (C₁ to C₆) or halogen (F, Cl, Br),

pyridyl, pyrazyl or pyrimidyl, which can be
5 unsubstituted or mono- to tetrasubstituted by alkyl (C₁ to C₆), alkoxy groups (C₁ to C₆) or halogen (F, Cl, Br).

The intermediate of the general formula (II):

10



where R¹ and R² each, individually or jointly, have the following meanings:

R¹, R²: H, alkyl having from 1 to 6 C atoms and tri-alkylsilyl (containing alkyl C₁ to C₆),

R³-R⁶ can each, individually or pairwise, being directly linked or not directly linked to one another via a single or double bond, have the following meaning:

- 15 1. alkyl (C₁ to C₆), alkyloxy (C₁ to C₆) or halogen (F, Cl, Br).
2. an aromatic ring from the groups

phenyl, naphthyl, anthracenyl or phenanthrenyl, which
20 can be unsubstituted or mono- to hexasubstituted by alkyl (C₁ to C₆), alkoxy groups (C₁ to C₆) or halogen (F, Cl, Br),

pyridyl, pyrazyl or pyrimidyl, which can be unsubsti-
25 tuted or mono- to tetrasubstituted by alkyl (C₁ to

C₆), alkoxy groups (C₁ to C₆) or halogen (F, Cl, Br),

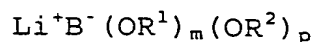
can be synthesized in yields of between 80 and 90%.

5

The end product of the general formula (I) can be used in electrolytes of lithium batteries, either on its own or in combination with other lithium salts and/or borate complexes. In so doing it is important to make
10 sure that the level of sodium-containing impurities is very low. Given the electrochemical properties (sodium is baser than lithium), sodium ions would otherwise be inserted into the structure of the negative electrodes. Ultimately this results in failure of the battery. The
15 method according to the invention can dispense with the use of sodium.

Consequently, the lithium borate complexes prepared according to the invention are suitable in particular
20 for use in electrochemical cells. The lithium borate complexes can be used, together with other lithium salts or alternatively with borate complexes, in electrolytes for secondary lithium batteries.

25 Alternatively, the lithium borate complexes can also be used in electrolytes comprising conventional conducting salts. Suitable, for example, are electrolytes comprising conducting salts selected from the group LiPF₆, LiBF₄, LiClO₄, LiAsF₆, LiCF₃SO₃, LiN(CF₃SO₂)₂ or
30 LiC(CF₃SO₂)₃ and mixtures of these. The electrolytes may also comprise organic isocyanates (DE 199 44 603) to reduce the water content. Equally, the electrolytes can comprise organic alkali metal salts (DE 199 10 968) as an additive. A suitable example is that of alkali metal
35 borates of the general formula



where

m and p are 0, 1, 2, 3 or 4, with $m+p=4$, and
 R^1 and R^2 are identical or different,

are linked or not linked directly to one another via a
5 single or double bond,

each, individually or jointly, have the meaning of an
aromatic or aliphatic carboxylic, dicarboxylic or
sulfonic acid radical, or

10

each, individually or jointly, have the meaning of an
aromatic ring from the group phenyl, naphthyl,
anthracenyl or phenanthrenyl which can be unsubstituted
or mono- to tetrasubstituted by A or Hal, or

15

each, individually or jointly, have the meaning of a
heterocyclic aromatic ring from the group pyridyl,
pyrazyl or bipyridyl, which can be unsubstituted or
mono- to trisubstituted by A or Hal, or

20

each, individually or jointly, have the meaning of an
aromatic hydroxy acid from the group of aromatic
hydroxy carboxylic acids or aromatic hydroxy sulfonic
acids, which can be unsubstituted or mono- to tetra-

25

substituted by A or Hal,

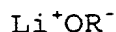
and

Hal is F, Cl or Br

30

and

A is alkyl which has from 1 to 6 C atoms and can
be mono- to trihalogenated. Equally suitable are alkali
35 metal alcoholates of the general formula



where R

has the meaning of an aromatic or aliphatic carboxylic, dicarboxylic or sulfonic acid radical, or

5 has the meaning of an aromatic ring from the group phenyl, naphthyl, anthracenyl or phenanthrenyl which can be unsubstituted or mono- to tetrasubstituted by A or Hal, or

10 has the meaning of a heterocyclic aromatic ring from the group pyridyl, pyrazyl or bipyridyl, which can be unsubstituted or mono- to trisubstituted by A or Hal, or

15 has the meaning of an aromatic hydroxy acid from the group of aromatic hydroxy carboxylic acids or aromatic hydroxy sulfonic acids, which can be unsubstituted or mono- to tetrasubstituted by A or Hal,

and

20

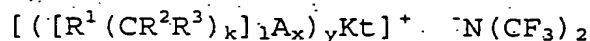
Hal is F, Cl or Br

and

25 A is alkyl which has from 1 to 6 C atoms and can be mono- to trihalogenated.

Equally, the electrolytes can comprise compounds of the following formula (DE 199 41 566)

30



where

35 Kt = N, P, As, Sb, S, Se

A = N, P, P(O), O, S, S(O), SO₂, As, As(O), Sb, Sb(O)

R^1 , R^2 and R^3 , identically or differently, are
H, halogen, substituted and/or unsubstituted alkyl
 C_nH_{2n+1} , substituted and/or unsubstituted alkenyl having
1-18 carbon atoms and one or more double bonds, substi-
5 tuted and/or unsubstituted alkynyl having 1-18 carbon
atoms and one or more triple bonds, substituted and/or
unsubstituted cycloalkyl C_mH_{2m-1} , mono- or polysubsti-
tuted and/or unsubstituted phenyl, substituted and/or
unsubstituted heteroaryl,

10

A can be included in various positions in R^1 , R^2 and/or
 R^3 ,

Kt can be included in cyclic or heterocyclic rings,

15

the groups bound to Kt can be identical or different,

where

20

$n = 1-18$

$m = 3-7$

$k = 0, 1-6$

$l = 1$ or 2 in the case of $x=1$ and 1 in the case $x=0$

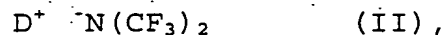
$x = 0, 1$

25

$y = 1-4$.

The method of preparing these compounds is character-
ized in that an alkali metal salt of the general
formula

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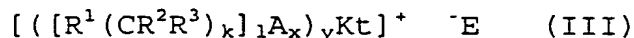


D^+ being selected from the group of the alkali metals,

is reacted in a polar organic solvent with a salt of

35

the general formula

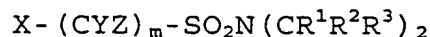


where

Kt, A, R¹, R², R³, k, l, x and y have the abovementioned meanings and

5 E is F⁻, Cl⁻, Br⁻, I⁻, BF₄⁻, ClO₄⁻, AsF₆⁻, SbF₆⁻ or PF₆⁻.

It is equally possible, however, to employ electrolytes comprising compounds of the general formula
10 (DE 199 53 638)



where

15

X is H, F, Cl, C_nF_{2n+1}, C_nF_{2n-1}, (SO₂)_kN(CR¹R²R³)₂

Y is H, F, Cl

Z is H, F, Cl

R¹, R², R³ are H and/or alkyl, fluoroalkyl, cycloalkyl

20 m is 0-9 and if X=H, m≠0

n is 1-9

k is 0, if m=0, and k=1 if m=1-9,

prepared by reacting partially fluorinated or per-
25 fluorinated alkylsulfonyl fluorides with dimethylamine in organic solvents and complex salts of the general formula (DE 199 51 804)

30 where $M^{x+}[EZ]_{x/y}^{y-}$

x, y are 1, 2, 3, 4, 5, 6

M^{x+} is a metal ion

35

E is a Lewis acid selected from the group
BR¹R²R³, AlR¹R²R³, PR¹R²R³R⁴R⁵, AsR¹R²R³R⁴R⁵, VR¹R²R³R⁴R⁵,

R^1 to R^5 are identical or different and are directly linked or are not directly linked to one another via a single or double bond, each, individually or jointly, have the meaning:

5

of a halogen (F, Cl, Br),

10

of an alkyl or alkoxy radical (C_1 to C_8) which may be partially or completely substituted by F, Cl, Br,

15

of an aromatic ring which is bound or not bound via oxygen, is selected from the group phenyl, naphthyl, anthracenyl or phenanthrenyl, and can be unsubstituted or mono- to hexasubstituted by alkyl (C_1 to C_8) or F, Cl, Br,

20

of an aromatic heterocyclic ring which is bound or not bound via oxygen, is selected from the group pyridyl, pyrazyl or pyrimidyl, and can be unsubstituted or mono- to tetrasubstituted by alkyl (C_1 to C_8) or F, Cl, Br, and

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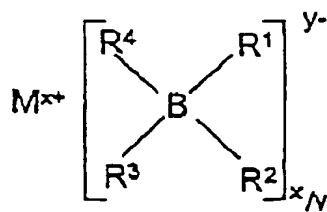
Z is OR^6 , NR^6R^7 , $CR^6R^7R^8$, OSO_2R^6 , $N(SO_2R^6)(SO_2R^7)$, $C(SO_2R^6)(SO_2R^7)(SO_2R^8)$, $OCOR^6$, where

30

R^6 to R^8 are identical or different, are directly linked or not directly linked to one another via a single or double bond, and each, individually or jointly, have the meaning of a hydrogen or the meaning as R^1 to R^5 , prepared by reacting an appropriate boron or phosphorus Lewis acid solvent adduct with a lithium or tetraalkylammonium imide, methanide or triflate.

35

Also present can be borate salts (DE 199 59 722) of the general formula



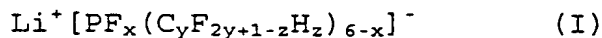
where

5 M is a metal ion or tetraalkylammonium ion,

x, y are 1, 2, 3, 4, 5 or 6,

R¹ to R⁴ are identical or different alkoxy or carboxy
 10 radicals (C₁ to C₈) which are directly linked or are not
 directly linked to one another via a single or double
 bond. These borate salts are prepared by reacting
 lithium tetraalcoholate borate or a 1:1 mixture of
 lithium alcoholate with a boric acid ester in an
 15 aprotic solvent with a suitable hydroxyl or carboxyl
 compound in a ratio of 2:1 or 4:1.

The additives can also be employed in electrolytes
 which comprise lithium fluoroalkyl phosphates of the
 20 general formula (I),



where

25

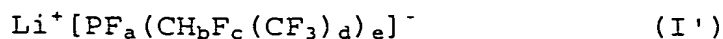
$$1 \leq x \leq 5$$

$$3 \leq y \leq 8$$

$$0 \leq z \leq 2y + 1$$

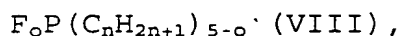
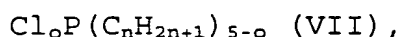
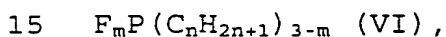
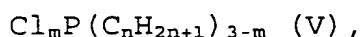
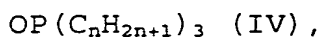
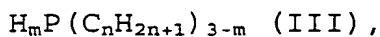
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and the ligands (C_yF_{2y+1-z}H_z) can be identical or
 different, with the exception of the compounds of the
 general formula (I'),



in which a is an integer from 2 to 5, $b = 0$ or 1, $c = 0$ or 1, $d = 2$ and

e is an integer from 1 to 4, with the conditions that b and c are not simultaneously = 0 and the sum $a + e$ equals 6 and the ligands $(CH_bF_c(CF_3)_d)$ are identical or different (DE 100 089 55). The method for preparing lithium fluoroalkyl phosphates of the general formula (I) is characterized in that at least one compound of the general formula



in each of which

$$0 \leq m \leq 2, \quad 3 \leq n \leq 8 \text{ and } 0 \leq o \leq 4,$$

is fluorinated by electrolysis in hydrogen fluoride, the fluorination product mixture thus obtained is separated by extraction, phase separation and/or distillation, and the fluorinated alkylphosphorane thus obtained is reacted with lithium fluoride in an aprotic solvent or solvent mixture with the exclusion of moisture, and the salt thus obtained of the general formula (I) is purified and isolated in accordance with standard procedures.

The additives can be employed in electrolytes for electrochemical cells which comprise anode material consisting of coated metal cores selected from the group Sb, Bi, Cd, In, Pb, Ga and tin or alloys of these (DE 100 16 024). The method for preparing said anode material is characterized in that

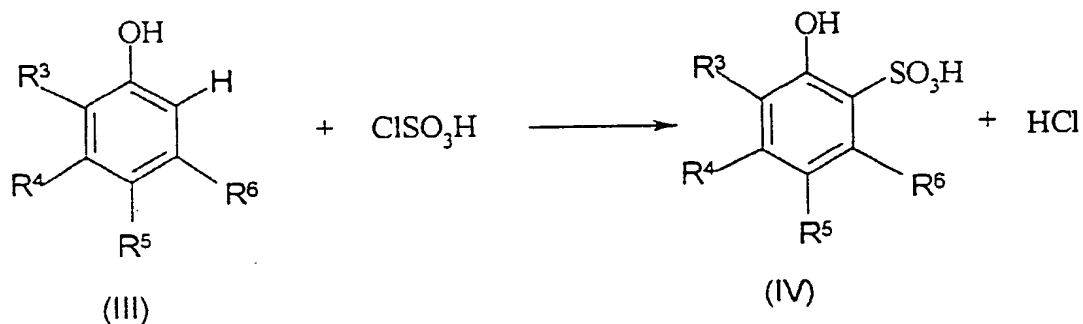
- a) a suspension of a sol of the metal core or alloy core is prepared in urotropine,
- b) the suspension is emulsified with C₅-C₁₂ hydrocarbons,
- c) the emulsion is precipitated onto the metal cores or alloy cores, and
- d) the metal hydroxides or oxihydroxides are converted into the corresponding oxide by annealing the system.

The additives can also be used in electrolytes for electrochemical cells comprising cathodes of standard lithium intercalation and insertion compounds, but alternatively comprising cathode materials which consist of lithium mixed oxide particles which are coated with one or more metal oxides (DE 199 22 522), by suspending the particles in an organic solvent, admixing the suspension with a solution of a hydrolysable metal compound and a hydrolysis solution and then filtering off the coated particles, drying them and calcining them if required. Alternatively, they can consist of lithium mixed oxide particles which are coated with one or more polymers (DE 199 46 066), obtained by a method in which the particles are suspended in a solvent and the coated particles are then filtered off, dried and calcined if required. Equally, the additives according to the invention can be used in systems comprising cathodes which consist of lithium mixed oxide particles, which are singly or multiply coated with alkali metal compounds and metal oxides (DE 100 14 884). The method for preparing these materials is characterized in that the particles are suspended in an organic solvent, an alkali metal salt compound suspended in an organic solvent is added, metal oxides dissolved in an organic solvent are added, the suspension is admixed with a hydrolysis solution,

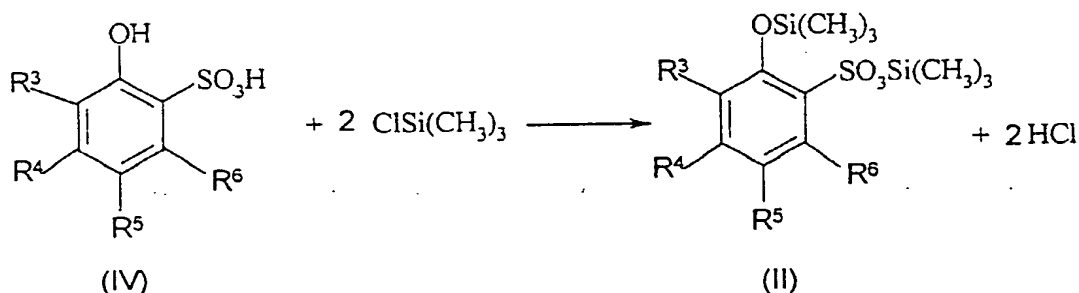
and the coated particles are then filtered off, dried and calcined.

A general example of the invention is explained below
5 in more detail.

Preparation of the intermediate (II):



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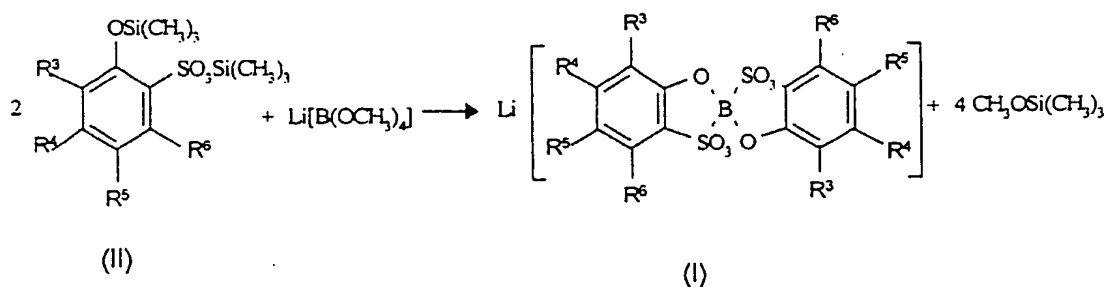
3-, 4-, 5-, 6-substituted phenol (III) is dissolved in
15 a suitable solvent under an inert gas atmosphere (argon
or nitrogen). This solution is admixed, over a period
of from 30 min to 2 hours at temperatures of between 10
and 30°C, preferably at room temperature, with a 5-20%
excess of chlorosulfonic acid. The precipitated product
(IV) is filtered off with suction under an inert gas
20 atmosphere after a reaction time of from 20 to 40
hours, as a rule after 24 hours, is washed with a
suitable solvent and dried in vacuo.

This intermediate (IV) is admixed under an inert gas
25 atmosphere with a 1.5 to 4-fold excess of the
stoichiometric amount of chlorotrimethylsilane and is

heated to boiling. After the vigorous release of HCl has died down, the same amount of chlorotrimethylsilane is added again and the solution is heated under reflux for 50-100 hours. The precipitated starting material is
 5 filtered off after cooling under an inert gas atmosphere. The excess chlorotrimethylsilane is removed at slightly reduced pressure and the intermediate of the general formula (II) is isolated by fractional distillation.

10

Conversion to the lithium complex salt:



15

To prepare the lithium complex salt (I), lithium tetraalcoholatoborate is introduced as initial charge in a polar aprotic solvent under an inert gas atmosphere. The solvent used can be a solvent from the
 20 group acetonitrile, acetone, nitromethane, dimethylformamide, dimethylacetamide, dimethyl sulfoxide, dimethyl carbonate, diethyl carbonate, propylene carbonate, butylene carbonate and methyl ethyl carbonate. After the addition of stoichiometric amounts
 25 of the intermediate (II) the mixture is stirred for from about half an hour to about 5 hours, preferably from about 45 min to about 90 min, at temperatures of between about 40 and about 70°C. The silane formed and the solvent are removed under slightly reduced pressure
 30 and the crude product is dried to constant weight in vacuo. The crude product is recrystallized from a suitable solvent or solvent mixture and then dried to constant weight in vacuo.

Without further elaboration, it is believed that one skilled in the art can, using the preceding description, utilize the present invention to its fullest extent. The following preferred specific
5 embodiments are, therefore, to be construed as merely illustrative, and not limitative of the remainder of the disclosure in any way whatsoever.

10 In the foregoing and in the following examples, all temperatures are set forth uncorrected in degrees Celsius; and, unless otherwise indicated, all parts and percentages are by weight.

15 The entire disclosure of all applications, patents and publications, cited above, and of corresponding German application No. 199 32 317.8, filed July 10, 1999 is hereby incorporated by reference.

20

Examples

Example 1

5-Fluoro-2-hydroxybenzenesulfonic acid

25

200 g (1.78 mol) of 4-fluorophenol are dissolved under a nitrogen atmosphere in 1300 ml of CHCl_3 (distilled, dried over CaCl_2). Added dropwise to this solution, over a period of 1 hour at room temperature with
30 stirring, are 131 ml (229 g = 1.96 mol) of chlorosulfonic acid, a vigorous release of HCl being observed initially, which dies down 30 min after completion and ceases entirely after a further 3 hours. After a reaction time of 24 hours, the precipitated product is
35 filtered off with suction at room temperature under inert gas, washed twice with 200 ml of CHCl_3 each time, and dried in vacuo at 1333 Pa and room temperature for 3 hours.

The product is a greyish-white, highly hygroscopic powder.

Yield: 302 g (88%)

5 Melting point: 110-114°C (sealed capillary)

^1H -NMR (250 MHz, $[\text{D}_6]$ DMSO):

δ = 6.77 (dd, $^3\text{J}_{\text{H}_3-\text{H}_4}=8.9$ Hz, $^4\text{J}_{\text{H}_3-\text{F}}=4.6$ Hz, 1H, H-3),

7.04 (dt, $^3\text{J}_{\text{H}_4-\text{H}_3}=8.9$ Hz, $^4\text{J}_{\text{H}_4-\text{H}_6}=3.3$ Hz, $^3\text{J}_{\text{H}_4-\text{F}}=8.9$ Hz, 1H, H-4),

10 7.16 (dd, $^3\text{J}_{\text{H}_6-\text{F}}=8.4$ Hz, $^4\text{J}_{\text{H}_6-\text{H}_4}=3.3$ Hz, 1H, H-6),

12.32 (br. s, 2H, OH, SO_3H)

^{13}C -NMR (62.9 MHz, $[\text{D}_6]$ DMSO):

δ = 113.46 (+, d, $^2\text{J}_{\text{C}-\text{F}}=24.0$ Hz, C-6),

118.47 (+, d, $^3\text{J}_{\text{C}-\text{F}}=7.4$ Hz, C-3),

15 118.53 (+, d, $^2\text{J}_{\text{C}-\text{F}}=23.0$ Hz, C-4)

131.79 (C_{quart} , d, $^3\text{J}_{\text{C}-\text{F}}=5.8$ Hz, C-1),

150.22 (C_{quart} , d, $^4\text{J}_{\text{C}-\text{F}}=1.8$ Hz, C-2),

155.10 (C_{quart} , d, $^1\text{J}_{\text{C}-\text{F}}=236.3$ Hz, C-5)

MS (70 eV, EI), m/z (%):

20 194 (2) $[\text{M}^++2]$, 193 (3) $[\text{M}^++1]$, 192 (54) $[\text{M}^+]$, 174 (44),

126 (23), 110 (65), 98 (15), 82 (100), 63 (16), 57 (20)

$\text{C}_6\text{H}_5\text{O}_4\text{FS}$: obs. 191.9892 (correct HRMS)

Example 2

25

Trimethylsilyl 5-fluoro-2-trimethylsilyloxy-benzene-sulfonate

302 g (1.57 mol) of 5-fluoro-2-hydroxybenzenesulfonic
30 acid are admixed, under an inert gas atmosphere at room
temperature with stirring, with 794 ml (683 g, 6.28
mol) of chlorotrimethylsilane, and the mixture is
heated to boiling. After the vigorous release of HCl
has died down, a further 794 ml of
35 chlorotrimethylsilane are added and the turbid solution
is heated under reflux for 96 hours. After cooling, the
precipitate is filtered off under inert gas, the excess
chlorotrimethylsilane is removed at 40-50°C under
slightly reduced pressure (about 4000 Pa) and the

product is obtained by fractional distillation in vacuo.

The product is a colorless, viscous, readily
5 hydrolysable liquid.

Yield: 496 g (93%)

Boiling point: 93-96°C/1.333 Pa

¹H-NMR (250 MHz, CDCl₃):

10 δ = 0.32 (s, 9H, OTMS),
0.36 (s, 9H, OTMS),
6.87 (dd, ³J_{H3-H4}=9.0 Hz, ⁴J_{H3-F}=4.3 Hz, 1H, H-3),
7.16 (ddd, ³J_{H4-H3}=9.0 Hz, ⁴J_{H4-H6}=3.2 Hz, ³J_{H4-F}=7.6 Hz, 1H,
H-4),

15 7.57 (dd, ⁴J_{H6-H4}=3.2 Hz, ³J_{H6-F}=8.0 Hz, 1H, H-6)

¹³C-NMR (62.9 MHz, CDCl₃):

δ = 0.38 (+, OTMS),
0.43 (+, OTMS),
116.23 (+, d, ²J_{C-F}=26.4 Hz, C-6),
20 121.08 (+, d, ²J_{C-F}=23.0 Hz, C-4),
121.70 (+, d, ³J_{C-F}=7.4 Hz, C-3),
130.99 (C_{quart}, d, ³J_{C-F}=7.3 Hz, C-1),
149.82 (C_{quart}, d, ⁴J_{C-F}=2.6 Hz, C-2),
155.77 (C_{quart}, d, ¹J_{C-F}=243.2 Hz, C-5)

25 MS (70eV, EI), m/z (%): 336 (3) [M⁺], 321 (33), 264
(43), 249 (60), 233 (96), 169 (39), 147 (59), 75 (100),
73 (76), 45 (18)

C₁₂H₂₁O₄FSSi₂: obs. 336.0683 (correct HRMS)

30 Elemental analysis: %C %H
calculated: 42.82 6.29
observed: 42.57 6.30

Example 3

35

Lithium bis[5-fluoro-2-olato-benzenesulfonato(2-)O,O']-
borate(1-)

2.81 g (19.8 mmol) of lithium tetramethanolato-
borate(1-) are suspended under inert gas in 100 ml of
dimethyl carbonate (DMC). Addition of 13.35 g
(39.7 mmol) of trimethylsilyl 5-fluoro-2-
5 trimethylsilyloxy-benzenesulfonate results in a clear
solution. This is kept at 45-50°C for one hour,
becoming slightly turbid in the process. The silane
formed is stripped off together with the solvent at
50°C under slightly reduced pressure, and the crude
10 product obtained is dried for 24 hours at 70°C in an
oil pump vacuum. The crude product is recrystallized
four times from toluene/DMC. Clouding observed during
the first two purification steps is removed by
filtration via a glass frit. The lithium salt is dried
15 to constant weight in vacuo at from 1 to 10 Pa at a
temperature of 70°C.

The product is obtained in the form of colorless
acicular crystals.

20

$^1\text{H-NMR}$ (250 MHz, $[\text{D}_6]$ DMSO):

δ = 7.08 (dd, $^3\text{J}_{\text{H}_3-\text{H}_4}=8.9$ Hz, $^4\text{J}_{\text{H}_3-\text{F}}=4.4$ Hz, 2H, H-3,
H-3'),

7.40 (dt, $^3\text{J}_{\text{H}_4-\text{H}_3}=8.9$ Hz, $^4\text{J}_{\text{H}_4-\text{H}_6}=3.2$ Hz, $^3\text{J}_{\text{H}_4-\text{F}}=8.9$ Hz, 2H,
25 H-4, H-4'),

7.50 (dd, $^4\text{J}_{\text{H}_6-\text{H}_4}=3.2$ Hz, $^3\text{J}_{\text{H}_6-\text{F}}=8.9$ Hz, 2H, H-6, H-6')

$^{13}\text{C-NMR}$ (62.9 MHz, $[\text{D}_6\text{DMSO}]$):

δ = 110.6 (+, d, $^2\text{J}_{\text{C}-\text{F}}=25.7$ Hz, C-6),

121.3 (+, d, $^2\text{J}_{\text{C}-\text{F}}=22.9$ Hz, C-4)

30 121.4 (+, d, $^3\text{J}_{\text{C}-\text{F}}=7.9$ Hz, C-3)

125.3 (C_{quart} , $^3\text{J}_{\text{C}-\text{F}}=7.6$ Hz, C-1)

148.9 (C_{quart} , $^4\text{J}_{\text{C}-\text{F}}=2.2$ Hz, C-2)

155.2 (C_{quart} , $^1\text{J}_{\text{C}-\text{F}}=240.0$ Hz, C-5)

35 AAS: Lithium content:

Calculated: 1.74% Observed: 1.75%

Example 4

Oxidation resistance of lithium bis[5-fluoro-2-olato-
5 benzenesulfonato(2-)O,O']borate(1-)

A measuring cell comprising a platinum working elec-
trode, lithium counterelectrode and lithium reference
electrode was used to record, in each case, 5
10 cyclovoltammograms successively. To do this, the poten-
tial, starting from the rest potential, was first
increased at a rate of 10 mV/s to 5 V against Li/Li⁺
and subsequently run back to the rest potential.

15 Electrolyte: 0.42 mol/kg_{Li} lithium bis[5-fluoro-2-olato-
benzenesulfonato(2-)O,O']borate(1-) EC/DMC (1:1)

The oxidation potential was measured as 4.5 V against
Li/Li⁺.

20

The preceding examples can be repeated with similar
success by substituting the generically or specifically
described reactants and/or operating conditions of this
invention for those used in the preceding examples.

25

From the foregoing description, one skilled in the art
can easily ascertain the essential characteristics of
this invention and, without departing from the spirit
and scope thereof, can make various changes and
30 modifications of the invention to adapt it to various
usages and conditions.